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[Title of the Invention]
    Fats and oils or oil selective absorbent material and oily water separator with the use of it

[Abstract]
[Problem to be Solved]
    The purpose of the present invention is to provide the oil selective absorbent and the oily water separator which can sufficiently remove in a short period of time fats and oils on the solid surface or in waste water including emulsion of water and oil.

[Solution]
    The fats and oils selective absorbent consisting of polyolefin microporous membrane made of super-high-molecular polyolefin or its polyolefin
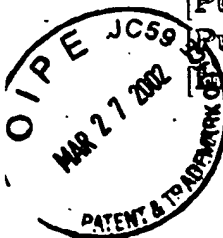
composition, having a specified porosity and through-hole diameter, the laminated material ●ng the same and the oily water s●rator in which these are packed into a porous vessel.

[Claims]
[Claim 1] The fats or oils selective absorbent consisting of a polyolefin microporous membrane made of a polyolefin or a polyolefin composition including the same which weight average molecular weight is equal to or more than 5×10^5, porosity is in the range of 30-95% and average through-hole diameter is in the range of 0.001-1μm.

[Claim 2] In the oil selective absorbent according to claim 1, the fats and oils selective absorbent in which the said polyolefin microporous membrane is a film-shaped, strip-shaped, chip-shaped or corrugate-shaped membrane.

[Claim 3] The oil selective absorbent which the oil selective absorbent according to claim 1 or claim 2 are laminated with a porous base material.

[Claim 4] The oily water separator which the oil selective absorbent according to either term of claim 1 through 3 is packed in a porous vessel and provided with a feed water pipe in the packing material.

[Detailed Description of the Invention]
[0001]
[Technical Field of the Invention]
The present invention relates to the fats and oils selective absorbent consisting of a polyolefin microporous membrane including super-high-molecular polyolefin or its composition, the oil selective absorbent consisting of its laminated material and the oily water separator using the same, especially, relates to the fats and oils selective absorbent and the oily water separator which absorbs fats and oils on a solid surface and oils in a waste water.
[0002]
[Prior Art]
Various kinds of mean are used conventionally to separate and remove fats and oils on a solid surface or in oil contaminated waste water. For example, "cosmetic face paper" made of paper is used to catch fats and oils of skin surface in case of makeup rectification, but absorbed amount per once is not always enough for it , therefore it is necessary to employ foundation garment, thus, "cosmetic face paper with the face powder" is marketed. In addition, various kinds of product is marketed in order to wipe and remove the oil which stuck to hand or solid surface of metal, but it was difficult to remove completely the oil in a short period of time by wiping with these products only.
[0003] On the other hand, in removing treatment for the oil which dispersed in water such as various industrial effluent, ballast water of ship, waste water of gas station, etc., an adsorption process is utilized in parallel with coagulating sedimentation, acid digestion, membrane separation method and the like. In this adsorption process, various kinds of organic, inorganic porous body and organic fiber body are employed. As a separation method for oil in liquid, there are disclosures, for example, of a method to filter-out and/or to make coagulate an oil drop by treating liquid including a fine oil drop with microporous

membrane having average pore diameter of 0.01-10μm (Japanese Patent Laid-Open No. S51-1314●●, of a separation device comprising the separation element which were made a cylindrical shape by winding a thermoplastic resin fine porous sheet on the inside and the surface of porous body (Japanese Patent Laid-Open No.S53-2390), of a method to permeate and separate oil selectively by contacting the treated water emulsion liquid incorporated oil with the porous membrane surface in which porosity is in the range of 1□5%, critical surface tension of membrane surface is less than 35dyn/cm to 20dyne/cm or more, average pore diameter is in the range of 0.03□5μm, pore diameter distribution is 1.5 or less, and the relation of average particle size of emulsion (γE) with the said average pore diameter of emulsion (γ) is 2γE□γ (Japanese Patent Laid-Open No.S55-79011).

[0004] However, a conventional selective adsorption or a separation method of oil in liquid can employ for this purpose, but the adsorption rate or the like was not always enough. Furthermore, it was not easy to determine extent of oil adsorption.

[0005]
[Problem to be Solved by the Invention]
The purpose of the present invention is to provide the fats and oil or oil selective absorbent and the oily water separator which can be sufficiently removed in a short period of time fats and oils on a solid surface or in waste water including emulsion of oil in water. Furthermore, it is to provide product of the oil selective absorption body which can determine extend of fats and oils or oil adsorption with visual observation easily.

[0006]
[Means to Solve the Problem]
In order to solve the above purpose, as a result of research of the present invention persons, it turn up that the specific microporous membrane which constitutes of a super-high-molecular polyolefin or a composition containing its component and its laminate are excellent as fats and oils or an oil selective absorbent, it become transparent when the oil was absorbed, and the oily water separator packed it into a porous vessel exhibits the performance excellent in separation of oil in a waste water.

[0007] That is, fats and oils or oil selective absorbent according to claim 1 of the present invention consists of polyolefin having weight average molecular weight of 5×10^5 or more, or a polyolefin composition containing its component, and constitutes of a polyolefin microporous membrane that a porosity is in the range of 30□95% and an average through-hole diameter is in the range of 0.001□1μm.

[0008] Moreover, the oil selective absorbent according to claim 2 of the present invention is constituted by laminating the oil selective absorbent according to claim 1 with porous base material.

[0009] Moreover, the oily water separator of the present invention which oil selective absorbent according to claim 1 or claim 2.is packed in a porous vessel and is provided with a feed pipe in the packing material.

[0010]
[Configuration for Carrying out the Invention]
The polyolefin microporous membrane which forms fats and oils or oil selective absorbent according to claim 1 of the present invention is described first. This polyolefin microporous membrane has a porosity of 30□95%,

preferably 40□90%. If the porosity is less than 30%, the absorption rate of fats and oils or an oil is low, and also amounts of absorption is low, thus, it is not preferable. On the other hand, if it exceeds 95%, mechanical property of the membrane becomes inadequate and it is inferior to a practicality. Moreover, the diameter of an average through-hole is in the range of 0.001□1 μm, preferably 0.03□0.5μm. If a pore diameter is less than 0.001μm, the absorption rate of oil is slow , while, if it exceeds 1μm, absorption retention is difficult. Furthermore, when tensile strength at break is 500 kg/cm² or more, it cannot split easily due to high strength, thus it is preferable.

[0011] For the polyolefin which forms the polyolefin microporous membrane of the present invention, a weight average molecular weight is 5×10^5 or more, preferably in the range of from1×10^6 to 15×10^6. If a weight average molecular weight is less than 5×10^5, in the stretching process at the time of production of a polyolefin microporous membrane, the maximum draw ratio is low and therefore a polyolefin microporous membrane having said physical properties is not obtained. On the other hand, if an upper limit exceeds 15×10^6, although it is not especially limited, the moldability at the time of production of a polyolefin microporous membrane is inferior.

[0012] Moreover, the polyolefin microporous membrane of the present invention can be used the compositions of the super-high-molecular polyolefin had weight average molecular weight of 5×10^5, preferably in the range of from 1×10^6 to 15×10^6 and the polyolefin had weight average molecular weight of 1×10^5 or more to less than 5×10^5, in order to aim at a high-concentration of the polyolefin solution during manufacturing of the below-mentioned polyolefin microporous membrane, the porosity of the microporous membrane obtained, and improvement in strength.

The content of the super-high-molecular polyolefin in this polyolefin composition is 1 weight% or more, more preferably in the range of 10□70 weight% as per 100 weight% of the total polyolefin composition.

[0013]
As for the polyolefin, a crystalline homopolymer, a two-step polymer, copolymers or these blended polymer, etc. which is obtained by polymerizing ethylene, propylene, 1-butene, 4-methyl-pentene-1 or 1-hexene, etc. Among these, polypropylene and polyethylene are preferable and high density polyethylene ant its composition, etc. are preferable especially with respect to strength. Moreover, the low density polyethylene, long chain branch polyethylene, etc. are preferable with respect to texture.

[0014] For the preferable manufacturing method of the polyolefin microporous membrane of the present invention, the solution of polyolefin or a polyolefin composition is prepared by feeding good solvents to the above polyolefin or the polyolefin composition, and after extruding this solution from a die of an extruder into the shape of a sheet, it is cooled to form a gel composition, and to carry out heat-stretching for this gel composition, and to eliminate the residual solvent. To be more precise, the following method which is indicated by the Japanese Patent Laid-open No. H03-64334 bulletin is more specifically employable:

[0015] For example, the solution of the polyolefin or polyolefin composition used as a raw material is prepared by carrying out the heating dissolution of an above-mentioned polyolefin or polyolefin composition into a solvent. As for this solvent, it is not limited as long as especially polyolefin or a polyolefin

composition can be dissolved satisfactorily. For example, although the aliphatic or cyclic hydrocarbon such as nonane, decane, undecane, dodecane, liquid paraffin, or the mineral oil fraction having a boiling point corresponding to these, etc. is given, in order to obtain gel-like moldings with a stable solvent content, the nonvolatile solvent such as liquid paraffin is preferable. Heating dissolution is performed by intensive mixing or kneading by an extruder at the temperature which polyolefin or a polyolefin composition is dissolved completely. The temperature is preferably. in the range of 140□250□. Moreover, the concentration of the solution of polyolefin or a polyolefin composition is in the range of 10□80 weight%, preferably in the range of 10□50wt%. If the concentration is less than 10 weight%, a lot of solvents is required, thus it is not economical, and at the time of molding into the shape of a sheet, the sheet molding is difficult due to large swell or large neck-in at the die outlet. In addition, it is preferable to add an antioxidant in order to prevent oxidation of polyolefin or a polyolefin composition in heating dissolution.

[0016] Next, the heating solution of this polyolefin or a polyolefin composition is extruded preferably from a die. For the die, usually a rectangular sheet die is used, and also a double-cylindrical inflation die and the like can be used. The die gap at the time of using a sheet die is usually 0.1□5 mm, and an extrusion-molding temperature is in the range of 140□250□. In this case, the extrusion speed is usually in the range of from 20□30cm/min to 2□3m/min.

[0017] Thus, the solution extruded from the die in this way is formed into the gel-like structure by cooling. It is preferable that the cooling performs at the speed of 50□/min or more to the level of at least the gelation temperature or less . Generally, if a cooling speed is slow, and the higher order structure of the gel-like composition obtained become coarse and the pseudo cell unit which forms it will also become big, while if a cooling speed is high, it will become a dense cell unit. If a cooling speed is less than 50□/min, crystallinity is increased and a gel-like composition suitable for stretching cannot be formed. As for the cooling method, a method of making a cold blast, cooling water, and other cooling mediums contacting directly, a method of contacting with roll chilled with a refrigerant, and the like can be used. In addition, the solution extruded from the die may be taken up at a take-up ratio of preferably 1□10, more preferably 1□5 before cooling or under cooling. If a take-up ratio becomes 10 or more, a neck-in become large, and easy to cause a break at the time of stretching which is not preferable.

[0018] Then, the stretching of this gel-like moldings is performed. After heating gel-like moldings, the stretching is performed by using an usual tenter process, a roll process, a inflation process, a milling process, or these combination methods in a prescribed draw ratio. For the stretching, biaxial stretching is preferable although a constant width uniaxial stretching or a biaxial stretching is acceptable.

Moreover, in the case of a biaxial stretching in lengthwise and in lateral directions, simultaneous stretching both in lengthwise and in lateral or sequential stretching is acceptable. A stretching temperature is melting points +10□ or less of polyolefin or a polyolefin composition, preferably in the range from a crystal dispersion temperature to less than a crystal melting point. Moreover, although a draw ratio depends on the thickness of a raw sheet, the draw ratio is preferably 2 times or more, more preferably 3□30 times in a constant width uniaxial stretching. The surface draw ratio is preferably 10

times, more preferably 150400 times in biaxial stretching. If the surface draw ratio is less than 100 times, the stretching is insufficient, and the microporous membrane having high elasticity and high strength is not obtained. On the other hand, if the surface draw ratio exceeds 400 times, restrictions is caused in the stretching operation, etc.

[0019] From the obtained stretching moldings, the residual solvent is eliminated by cleaning with a solvent. As for a cleaning solvent, the volatile solvent such as hydrocarbons such as pentane, hexane, heptane; chlorinated hydrocarbons such as methylene chloride, carbon tetrachloride; fluorinated hydrocarbons such as trifluoroethane; ethers such as diethyl ether, dioxane can be used. These solvents are suitably selected according to the solvent used for dissolution of a polyolefin composition, and is used independently or as its mixture. The cleaning method can be performed by a method of dipping to and extracting by a solvent, a method showering the solvent, or a method by these combination.

[0020] The above cleaning is carried out until the residual solvent in stretching moldings becomes less than 1 weight%. Although a cleaning solvent is dried after that, drying of a cleaning solvent can be performed by such method as heating and air drying. As for dry stretching moldings, it is desirable to carry out heat setting within the temperature range between a crystal dispersion temperature and a melting point.

[0021] In the polyolefin microporous membrane manufactured as mentioned above, the porosity is 30 to 95%, the average diameter of a through-hole is 0.0010 1μm, and tensile strength at break is 500 kg/cm^2 or more. Moreover, although the thickness of a polyolefin microporous membrane is selected by the application, generally it is about 5-50μm.

[0022] The polyolefin microporous membrane obtained in this way can be used as fats and oils or oil selective absorbent in the shape of a film or of a strip and of a chip, or in the shape such as a thing subjected to a wrinkle processing mechanically or thermally. Since the polyolefin microporous membrane used for the oil selective absorbent of the present invention become transparent when fats and oils or oil is absorbed, the extent of oil absorption can be easily judged by visual observation. Moreover, it can be used in various fields from the repetition use by cleaning being possible.

[0023] The oil selective absorbent according to claim 2 of the present invention will now be explained. The oil selective absorbent according to claim 2 of the present invention is constituted by laminating the polyolefin microporous membrane which forms the oil selective absorbent according to claim 1 of the above with the porous base material.

[0024] As for the above-mentioned porous base material, the arbitrary fabric cloths made of a thermoplastic resin, a non-woven fabric, a porous film, a porous sheet, or a porous film, etc. which can be laminated with the polyolefin microporous membrane are given. Among these, a non-woven fabric made of a polyolefin, for example, a non-woven fabric having fiber diameter of 0.5 50μm is preferable with respect to laminating characteristic with the above-mentioned polyolefin microporous membrane.

[0025] In the laminating of the polyolefin microporous membrane and a porous base material, it is required not to spoil porosity of both materials. A preferable laminating method is calendering, embossing and the like, but, additionally a method of carrying out a surrounding welding or a surrounding intermittent

welding is also acce⬤ble. By such laminating, the abs⬤tion retention of oil is improved, and th⬤acticality in a usage can also be⬤roved.

[0026] Next, the oily water separator of the present invention is described herein. The oily water separator of the present invention is constituted by packing the above-mentioned oil selective absorbent according to claim 1 or claim 2 into a porous vessel and providing a feed pipe in the packing material.

[0027] As for the said porous vessel, the material or shape is not limited especially as long as the above-mentioned oil selective absorbent can be packed in. For example, a bag consisting of a fabric cloth or a non-woven fabric made of natural fiber or synthetic fiber, a vessel consisting of a mesh or a perforated plate made of a synthetic resin, and a vessel constituting of a metal mesh or a metal perforated plate are given. Moreover, the feed pipe of which inserted portion into the oil selective absorbent is made of a mesh or porous material is given.

[0028] This oily water separator is described in detail referring to a drawing of the
example. The oily water separator as shown in Figure-1, the porous container 2, for example, the mesh-like cylindrical vessel 2 made of stainless steel, is filled with an oil selective absorbent 1 up to the upper part, and the feed pipe 3, for example, the mesh-like pipe 3 made of stainless steel is inserted into the center section of the oil selective absorbent 1. The mixed waste water of oil and water is supplied from the above-mentioned feed pipe 3, and it flows through the packed oil selective absorbent 1 from the porous part, and oil is adsorbed by the oil selective absorbent 1, and purified water flows out of the hole of the porous vessel 2.

[0029]
[Examples] The present invention is illustrated in detail by the examples, however these examples are not to be construed to limit the scope of the invention.

Herein, the samples used are the following:
(1) Sample 1 (S-1): The polyethylene composition was obtained by adding 0.375 parts by weight of the antioxidant into 100 parts by weight of polyethylene composition consisting of 5.5 parts by weight of super-high-molecular polyethylene having a weight average molecular weight of 2.5×10^6 and 24.5 parts by weight of high-density polyethylene having a weight average molecular weight of 3.5×10^5.

This polyethylene composition of 30 parts by weight was supplied to a twin screw extruder (58mmφ, L/D=42, intensive mixing type). Moreover, the liquid paraffin of 70 parts by weight was supplied from the side feeder of this twin screw extruder, and kneaded to provide a polyethylene solution in the extruder.

[0030] Then, it extruded at 190□ from a T-die installed at the front end of this extruder, and the gel-like sheet was formed while taking up by a chill roll. Then, simultaneous biaxial stretching was performed from this gel-like sheet at a draw ratio of 5×5 at 115□ to obtain a stretched film. The obtained stretched film was washed with methylene chloride to extract and remove the residual liquid, and then was dried and heat treated. Thus, the polyethylene microporous membrane of which a porosity was 40% , an average diameter of the through-hole was 0.03μm and a thickness was 25μm is obtained.

(2) Sample 2 (S-2): The sample was obtained by cutting out the above-

mentioned polyeth   e microporous membrane into s   shape having a width of 2mm.

(3) Sample 3 (S-3): The sample was obtained by thermo-mechanically wrinkling processing from the above S-1.

(4) Sample 4 (S-4): The sample was obtained by sandwiching the above S-1 with two polypropylene non-woven fabrics of 50g/m² coating weight, and carrying out the heat welding on all sides.

(5) Sample 5 (S-5): The sample was obtained by sandwiching the above S-2 with two polypropylene non-woven fabrics of 50g/m² coating weight, and carrying out the heat welding on all sides.

(6) Sample 6 (S-6): "cosmetic face paper" on the market.

(7) Sample 7 (S-7): "a paper towel" made of pulp on the market.

(8) Sample 8 (S-8): Polypropylene non-woven fabric of 22 g/m² coating weight.

(9) Sample 9 (S-9): The sample obtained by cutting out the above S-6 into the strip having a width of 2mm.

(10) Sample 10 (S-10): The sample was obtained by cutting out the above S-7 into the strip having a width of 2mm.

(11) Sample 11 (S-11) : The sample obtained by cutting out the above S-8 into the shape of a strip having a width of 2mm.

[0031]

[Examples 1 through 5, and Comparative Examples 1 through 3]
On a glass plate, 1ml of paraffin oil with a viscosity of 45cps was dropped by a syringe, and the above-mentioned samples 1 through 8 were put on it, pressed lightly, and the absorptivity of oil was evaluated. The results are shown in Table-1.

[0032] Table-1

	Example 1	Example 2	Example 3	Example 4	Example 5
Samples	S-1	S-2	S-3	S-4	S-5
Absorptivity[1]	□	□	□	o	o

	Comparative Example 1	Comparative Example 2	Comparative Example 3
Samples	S-6	S-7	S-8
Absorptivity [1]	×	×	×

Absorptivity [1]: The mark □ became transparent by absorbing oil instantly, and residual oil was not detected on the glass plate and on the sample surface, but it was absorbed into the sample. The mark o was that residual oil was not detected on the glass plate, but was slightly detected on a sample surface. The mark × was that residual oil was detected on the glass plate, and a lot of oil adhesion was observed also on a sample surface.

[0033]

[Examples 6 through 8, and Comparative Examples 4 through 6]
An equal volumes of water and the above-mentioned paraffin oil were made into the fine distributed status by using a homogenizer, and this 1ml was dropped on glass plate, and samples 1 through 3, and 6 trough 8 were put on it, and pressed lightly, and the absorptivity of oil was evaluated. The results are shown in Table-2.

[0034] Table-2

	Example 6	Example 7	Example 8
Samples	S-1	S-2	S-3

Absorptivity(2)	Comparative Example 1	Comparative Example 2	Comparative Example 3
Samples	S-6	S-7	S-8
Absorptivity (2)	×	×	×

Absorptivity(2) : The mark □ became transparent by selectively absorbing oil instantly, a fine drop of water was observed on the sample surface and the glass plate, and oil was absorbed selectively. The mark × was that dispersed oil and water were detected on the sample surface and the glass plate and was no selective absorption of oil.

[0035]

[Example 9 and Comparative Examples 7 through 9]

The samples 2 and 9 through 11 of 10g, respectively, was packed into the mesh-like cylindrical vessel made of stainless steel as shown in Figure-1, and the stainless steel pipe of which its inserted portion was is a mesh-like shape and was inserted into the center, 100g of dispersed material (90g of water and 10g of said oil) was poured in from the upper end of the pipe, the liquids which ooze out from the above-mentioned mesh-like cylindrical vessel made of stainless steel were collected, and the water was evaporated in the evaporator, and the amount of a residue was measured. The results are shown in Table-3.

[0036] Table-3

	Example 9	Comparative Example7	Comparative Example 8	Comparative Example 9
Samples	S-2	S-9	S-10	S-11
Residue	10mg(-)	5.4g	3.7g	1.2g

In addition, each sample (S-2) after test was washed with a lot of hexane, then dried, evaluated repeatedly, and the same result was obtained.

[0037] Conclusively, as clearly indicated in Table -1 and -2, the oil selective absorbent of the present invention absorbs oil instantly, retains so much oil, and absorbs the oil selectively from the mixture of oil/water. Moreover, the oily water separator of the present invention can remove the oil from the mixture of oil/water almost completely as shown in Table-3.

[0038]

[Effect of the Invention]

As explained above in detail, the oil selective absorbent of the present invention can absorbed and retained selectively the fats and oils or oil on the solid surface, or the oil the mixture of oil/water so much in a short period of time. Moreover, the oily water separator can separate and eliminate efficiently the oil from the mixture of oil/water. Therefore, although it can be used in various fields, the oil selective absorbent is suitably used for a cosmetic face paper, oil wiping material, etc. Moreover, the oily water separator is useful to water purification oil-mixed waste water.

[Brief Description of the Drawing]

[Figure-1] Partly sectioned side view drawing of an example of the oily water separator of the present invention.

[Denomination of Reference Numerals]

1: Oil selective absorbent,
2: Porous vessel
3: Water feed pipe
3': Mesh-like portion of the water feed pipe.

Figure-1